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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷: C08F 2/26, C09D 157/06	A1	(11) International Publication Number: WO 00/27890 (43) International Publication Date: 18 May 2000 (18.05.00)
(21) International Application Number: PCT/GB99/03574 (22) International Filing Date: 28 October 1999 (28.10.99) (30) Priority Data: 9824267.0 6 November 1998 (06.11.98) GB 9913034.6 5 June 1999 (05.06.99) GB (71) Applicant (for all designated States except US): ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road West, Warley, West Midlands B68 0NN (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): HASLING, Peter, David [GB/GB]; 29 Clifton Street, Stourbridge, West Midlands DY8 3XR (GB). (74) Agent: BARKER BRETTELL; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYMERISABLE SURFACTANTS (57) Abstract <p>The invention provides a polymerisable surfactant having at least one hydrophobic polymerisable group which is linked by polyalkyleneoxy groups to a hydrophilic group, wherein the polymerisable surfactant is of the general formula: $(RCH = CR'COO[CH_2CHR''O]_x)_nPO(OY)_m$, where $n + m = 3$; x is between 5 and 40; $R = H$ or CH_3 or $COOR'''$; $R' = H$ or CH_3; $R'' = H$, CH_3 or C_2H_5; $R''' = C_1-C_{20}alkyl$; $Y = H$ or an alkali metal atom. The invention further relates to a method of making such surfactants and to their use in surface coatings, to improve water-resistance and to reduce the formation of "bloom" and "blush" in such coatings.</p>		

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/03574

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08F2/26 C09D157/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 325 662 A (SYNRES INT. B.V.) 22 April 1977 (1977-04-22) page 3, line 32 -page 4, line 27; claim 1 page 1, line 5 -page 1, line 12	1-31
A	US 3 855 364 A (R. STECKLER) 17 December 1974 (1974-12-17)	
A	EP 0 458 245 A (NIPPON PAINT CO.) 27 November 1991 (1991-11-27)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 January 2000

Date of mailing of the international search report

04/02/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/03574

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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POLYMERISABLE SURFACTANTS

The present invention relates to polymerisable surfactants comprising at least one hydrophobic polymerisable group which is linked by
5 polyalkyleneoxy groups to a hydrophilic group. The surfactants are particularly useful in emulsion-polymerised surface coatings. The present invention also relates to a method of making the polymerisable surfactants, to uses thereof, and to surface coatings including the surfactants.

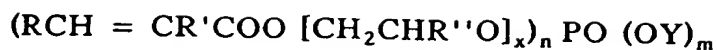
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Polymerisable surfactants are known in the art and have often been used in surface coatings. However, such prior-art surfactant-containing coatings have a tendency to absorb moisture resulting in partial detachment of the coating, a problem known as "bloom". The problem of
15 "blush", a whitening effect of a coating when subjected to prolonged immersion in water, is also evident in coatings containing prior-art surfactants.

The object of the present invention is to provide a polymerisable
20 surfactant which is particularly suitable for use in surface coatings, which has improved water resistance and which reduces the problems of "bloom" and "blush" in coatings. A method of making such a polymerisable surfactant is also provided.

25 According to a first aspect, the present invention provides a polymerisable surfactant having at least one hydrophobic polymerisable group which is linked by polyalkyleneoxy groups to a hydrophilic group, wherein the polymerisable surfactant is of the general formula:

2



where $n + m = 3$

x is between 5 and 40

R = H or CH₃ or COOR'''

5 R' = H or CH₃

R'' = H, CH₃ or C₂H₅

R''' = C₁ - C₂₀ alkyl

Y = H or an alkali metal atom

10 Preferably the hydrophobic polymerisable group represented by $RCH = CR'COO$ is acrylate or methacrylate, in which case R is hydrogen and R' is hydrogen or methyl respectively.

The hydrophobic polymerisable group may alternatively be maleate,
15 fumarate, crotonate or isocrotonate.

Preferably x is between 10 and 30, more preferably 17 and 22, most preferably x is 20.

20 Preferably the oxyalkylene groups represented by $[CH_2CHR''O]$ comprise mainly propyleneoxy groups. For example, from 80% - 100% of the oxyalkylene groups may be propyleneoxy groups. Preferably, at least 90%, more preferably at least 95% and most preferably at least 98% of the oxyalkylene groups are propyleneoxy groups.

25

The balance of the oxyalkylene groups not being propyleneoxy groups is preferably selected from ethyleneoxy or butyleneoxy groups.

30 The oxyalkylene groups as well as acting as linking groups, in fact form the main hydrophobe in the polymerisable surfactant.

Preferably the hydrophilic group represented by $\text{PO}(\text{OY})_m$ is a phosphate group, i.e. Y represents hydrogen. Alternatively, the hydrophilic group may be a water-soluble phosphate salt group, for example alkali metal phosphate, in which Y represents an alkali metal atom.

5

Although it is not intended that the present invention be construed with reference to any particular theory, it is believed that surfactants according to the present invention exhibit improved water-resistance in comparison with prior-art surfactants because they do not include a non-ionic hydrophilic group, such as polyethylene oxide. In many prior-art polymerisable surfactants, a hydrophilic non-ionic group is present which can give rise to poor water sensitivity in a final coating. Ionic groups are only hydrophilic when ionised and therefore the resultant dried coatings are less hydrophilic and less water sensitive than coatings including non-ionic hydrophiles.

15

According to a second aspect, the present invention provides a method of making a polymerisable surfactant according to the first aspect of the present invention, the method comprising the steps of:

20

reacting an unsaturated carboxylic acid corresponding to the hydrophobic group with an alkylene oxide corresponding to the oxyalkylene linking group while maintaining the temperature of the reaction below that at which spontaneous polymerisation of the unsaturated groups of the hydrophobic group would occur; and

25

phosphating the resultant polyalkoxylated hydrophobic group.

The polyalkoxylation process step may be carried out with the aid of a catalyst. The catalyst is preferably a catalyst for alkoxylation which does

30

not catalyse the polymerisation of unsaturated groups of the hydrophobic group.

5 A preferred catalyst for alkoxylation is a strong Lewis acid such as boron trifluoride.

10 Preferably, a portion, most preferably a small portion, of the catalyst for alkoxylation is added to the unsaturated carboxylic acid before the alkylene oxide. Preferably the bulk of the catalyst is added with the alkylene oxide. A remaining portion of the catalyst is preferably added after completion of addition of the alkylene oxide to maximise conversion as the catalyst has a short active life. Hydroquinone is preferably added to the reaction mixture after the addition of the remaining portion of the catalyst. The hydroquinone is added to inhibit autopolymerisation of the
15 unsaturated groups of the hydrophobic group. Any unreacted alkylene oxide may be removed, preferably by sparging with air.

20 Preferably, the reaction of the unsaturated carboxylic acid and the alkylene oxide is carried out in an inert atmosphere, for example under nitrogen. The reaction mixture may be stirred. Preferably, moisture is excluded from the reaction mixture. Preferably, the alkylene oxide is added continuously at a constant rate over a given time period, suitably 90 minutes.

25 The phosphorylation step is preferably carried out by means of phosphorus pentoxide. The most preferred form of phosphorus pentoxide is the solid form. The phosphorus pentoxide may be added over a given period of time, preferably one hour. Preferably, when addition of the phosphorus pentoxide is complete, the resulting mixture is maintained at an elevated
30 temperature, such as 80°C, for about 4 hours, with stirring.

Preferably, the product of the phosphation step is treated to remove any free phosphoric acid. The presence of phosphoric acid can be detrimental to the final product containing the surfactant. Deionised water may be used to wash the product.

5

According to a third aspect, the present invention provides a coating including a polymerisable surfactant according to the first or second aspect of the invention.

10 Preferably the coating is an acrylic coating, an acrylic or vinyl halide latex composition, a latex paint, a coating for contact lenses, a coating to modify the surface properties of organic polymers, glass, graphite, metals, a coating to convert hydrophilic articles to hydrophobic articles and vice versa, a coating for fabrics.

15

Preferably the coating is an emulsion polymerised coating.

The present invention also provides adhesives, flocculants, resinous binders, polymer materials for medical or dental use and oil-displacing
20 fluids including the polymerisable surfactant of the present invention.

Examples of the polyalkoxylation and phosphation steps are set out below:

Polyalkoxylations

25 Example 1

Polypropoxylate(20) Methacrylate (PP20M)

Reagents:

30

6

Methacrylic Acid:	28.3g	(0.329 mol)
Propylene oxide:	381.6g	(6.580 mol)
Boron trifluoride etherate:	5.0 ml	
Hydroquinone, monomethyl ether:	0.20 g	

5

A reactor comprising a 1-litre jacketed vessel fitted with overhead stirrer, septum cap, nitrogen bleed, condenser, peristaltic addition tube and thermometer was heated to 120°C for 1 hour under nitrogen and the flask lid flamed to ensure dryness. The reactor was then cooled to room temperature.

10

Methacrylic acid (28.3g, 0.329 mol) and boron trifluoride etherate (1.0 ml) were charged to the reactor (BF₃ by syringe/septum seal). Propylene oxide was then added to the stirred reaction mixture at a constant rate over 90 minutes, using a peristaltic pump. Starting at the same time, the remainder of the BF₃ was added over 120 minutes via a screw-feed syringe pump. Immediately the additions commenced the temperature rose to 40°C and the reactor jacket was cooled to - 5°C. Care was taken to ensure that the reaction temperature was maintained between 40 and 50°C throughout the propylene oxide addition.

15

20

After the addition of the propylene oxide was complete, the jacket temperature was raised to 50°C while the BF₃ addition was completed. When this addition was complete the nitrogen bleed was replaced with an air bleed and monomethylether hydroquinone (0.20g, 500 ppm) added. The jacket temperature was raised to 60°C and the clear, colourless product was sparged with air to remove any unreacted propylene oxide.

25

Example 2**Polypropoxylate(6) Methacrylate (PP6M)**

- 5 The procedure of Example 1 was followed, but with the following reagents:

	Methacrylic Acid:	28.3g	(0.329 mol)
	Propylene oxide:	114.5g	(1.974 mol)
10	Boron trifluoride etherate:	3.0 ml	
	Hydroquinone, monomethyl ether	0.07g	

Example 3

15 **Polypropoxylate(12) Methacrylate (PP12M)**

The procedure of Example 1 was followed, but with the following reagents:

20	Methacrylic Acid:	28.3g	(0.329 mol)
	Propylene oxide:	229.0g	(1.974 mol)
	Boron trifluoride etherate:	5.0 ml	
	Hydroquinone, monomethyl ether	0.13g	

25 **Example 4**

Polypropoxylate(28) Methacrylate (PP28M)

- 30 The procedure of Example 1 was followed, but with the following reagents:

8

Methacrylic Acid:	14.1g	(0.164 mol)
Propylene oxide:	266.3g	(4.592 mol)
Boron trifluoride etherate:	5.0 ml	
Hydroquinone, monomethyl ether	0.14g	

5

Example 5

Polybutoxylatepropoxylate(12) Methacrylate (PBP12M)

10 Reagents:

Methacrylic Acid:	28.3g	(0.329 mol)
Propylene oxide:	114.5g	(1.970 mol)
Butylene oxide:	142.0g	(1.970 mol)
15 Boron trifluoride etherate:	8.0 ml	
Hydroquinone, monomethyl ether	0.14g	

A reactor comprising a 1-litre jacketed vessel fitted with overhead stirrer, septum cap, nitrogen bleed, condenser, peristaltic addition tube and
20 thermometer was heated to 120°C for 1 hour under nitrogen and the flask lid flamed to ensure dryness. The reactor was then cooled to room temperature.

Methacrylic acid (28.3g, 0.329 mol) and boron trifluoride etherate (1.0
25 ml) were charged to the reactor (BF₃ by syringe/septum seal). Propylene oxide (114.5g) and butylene oxide (142.0g) were combined and added to the stirred reaction mixture at a constant rate over 90 minutes, using a peristaltic pump. Starting at the same time, the remainder of the BF₃ was added over 120 minutes, via a screw-feed syringe pump. Immediately the
30 additions commenced the temperature rose to 40°C and the reactor jacket

was cooled to -5°C . Care was taken to ensure that the reaction temperature was maintained between 40 and 50°C throughout propylene oxide and butylene oxide addition.

- 5 After the addition of propylene oxide/butylene oxide was complete, the jacket temperature was raised to 50°C while the BF_3 addition was completed. When this addition was complete the nitrogen bleed was replaced with an air bleed and monomethyl ether hydroquinone (0.14g , 500 ppm) added. The jacket temperature was raised to 60°C and the
- 10 clear, colourless product was sparged with air to remove any unreacted propylene oxide/butylene oxide.

Phosphation

Example 6

15

Polypropoxylate(20) Methacrylate Phosphate (PP20MP)

Reagents:

- 20 PP20M (Example 1): 260g (0.196 mol)
Phosphorus Pentoxide: 9.9g (0.081 mol)

- A 1 litre jacketed vessel fitted with overhead stirrer, air bleed, condenser, solid-addition inlet and thermometer was charged with PP20M (260g),
- 25 which was stirred vigorously whilst being heated to 60°C . Phosphorus pentoxide (9.9g) was added via the solid-addition inlet over 1 hour. The temperature was then raised to 80°C and the reaction mixture stirred at this temperature for a further 4 hours before being cooled. The yellow, oily product was then washed with distilled water until the pH of the
- 30 water washings rose to 3.0.

An example of the use of the polymerisable surfactant of Example 1 in an acrylic emulsion is set out below.

Example 7

5

Preparation of an Acrylic Latex Using PP20MP

Reagents:

10	Solution (1)	PP20MP (Example 1) :	5.6g
		Water:	290g
		Ammonia (37% aq)	0.5ml
15	Solution (2)	Methyl Methacrylate:	201g
		Butyl Acrylate:	162g
20	Solution (3)	Methacrylic Acid:	4.6g
		Ammonium Persulphate:	1.2g
		Water:	58g
		Ammonia (37%aq):	5.0ml
	Solution (4)	Ammonium Persulphate:	0.3g
		Water:	6g

25 A 2 litre resin pot fitted with nitrogen inlet, condenser, overhead stirrer and two peristaltic addition inlets was charged with solution (1). The milky solution was stirred at 350 rpm whilst being heated to 80°C under nitrogen. After 30 minutes 15g of solution (2), 3g of solution (3) and half of solution (4) was added. Almost immediately a blue tint was observed
30 indicating that polymerisation had commenced. After 5 minutes the

remainder of solutions (2) and (3) were added dropwise over 3.5 hours. Fifteen minutes after additions were completed the remainder of solution (4) was added and the emulsion left stirring for 1 hour at 80°C. The latex produced was cooled to room temperature and filtered through a 150 µm mesh.

Example 8

Preparation of a Comparative Latex Using an Industry Standard 10 Surfactant - Empimin*OT60

The procedure of Example 7 (above) was repeated using 5.6g Empimin OT60 (a dialkyl sulfosuccinate made by Albright & Wilson Limited) in place of PP20MP.

15

*Epimin is a Registered Trade Mark

Example 9

20 Comparison Test

A comparison of two polymer latices made by the method of Example 7, but using amounts of 1.5% and 3.0% weight with respect to total monomer weight of polymerisable surfactant with the control polymer latex made by the method of Example 8 was, carried out.

25

The comparison used three tests set out below:

(a) Gloss on mild steel

30

Emulsions were drawn on a film of a cleaned dry mild steel panel using a 100 μ bar. The coated panels were placed in an oven at 50°C overnight.

5 The gloss was measured at 20°C and 60°C using a Rhopoint
"Novo-Gloss" glossmeter.

(b) Foaming

10 25ml of each emulsion was diluted with an equal volume of deionised
water and placed in a 100 ml measuring cylinder and shaken for 30
seconds. The foam height is presented as a percentage of the initial liquid
height.

(c) Adhesion

15

Adhesion was tested on panels of mild steel and aluminium by applying
emulsion to the panels as described in (a) and according to BS 39000:
E6 : 1992.

20 The results of the above 3 tests are set out in Table 1 (below).

TABLE 1

Polymer	Gloss		Foam Height	Adhesion (x hatch and Peel)	
	60°C	20°C		Aluminium	Mild steel
Control	80	46.5	130	Complete removal	75% of squares removed
1.5% PP20MP	93.8	79.5	30	No removal	No removal
3.0% PP20MP	97.2	92.6	26	No removal	No removal

5 Comparison of the Latices

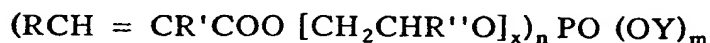
The polymer latex prepared in Example 7 having 1.5% and 3.0% polymer has been compared with that produced in Example 8. The coatings produced from dried films of the latices have also been compared.

10

The latex produced using PP20MP (Example 7) has higher gloss, reduced water- sensitivity and increased adhesion to aluminium and steel substrates than that prepared with Empimin OT60 (Example 8).

CLAIMS

1. A polymerisable surfactant having at least one hydrophobic polymerisable group which is linked by polyalkyleneoxy groups to a hydrophilic group, wherein the polymerisable surfactant is of the general formula:



where $n + m = 3$

- 10 x is between 5 and 40
 R = H or CH₃ or COOR'''
 R' = H or CH₃
 R'' = H, CH₃ or C₂H₅
 R''' = C₁ - C₂₀ alkyl
 15 Y = H or an alkali metal atom

2. A polymerisable surfactant according to Claim 1 wherein the hydrophobic polymerisable group represented by $RCH=CR'COO$ is acrylate.

20

3. A polymerisable surfactant according to Claim 1 wherein the hydrophobic polymerisable group represented by $RCH=CR'COO$ is methacrylate.

- 25 4. A polymerisable surfactant according to Claim 1 wherein the hydrophobic polymerisable group is maleate, fumarate, crotonate or isocrotonate.

5. A polymerisable surfactant according to any preceding claim
 30 wherein x is between 17 and 22.

6. A polymerisable surfactant according to Claim 5 wherein x is 20.
7. A polymerisable surfactant according to any preceding claim wherein the oxyalkylene groups represented by $[\text{CH}_2\text{CHR}''\text{O}]$ comprise
5 mainly propyleneoxy groups.
8. A polymerisable surfactant according to Claim 7 wherein from 80% - 100% of the oxyalkylene groups are propyleneoxy groups.
- 10 9. A polymerisable surfactant according to Claim 7 or 8 wherein the balance of the oxyalkylene groups not being propyleneoxy groups is selected from ethyleneoxy and butyleneoxy groups.
10. A polymerisable surfactant according to any preceding claim
15 wherein the hydrophilic group represented by $\text{PO}(\text{OY})_m$ is a phosphate group, where Y represents hydrogen.
11. A polymerisable surfactant according to any one of Claims 1-9 wherein the hydrophilic group represented by $\text{PO}(\text{OY})_m$ is a water-soluble
20 phosphate salt group.
12. A polymerisable surfactant according to Claim 11 wherein the water soluble phosphate salt is group is an alkali metal phosphate, in which Y represents an alkali metal atom.
25
13. A method of making a polymerisable surfactant according to any one of Claims 1 to 12, the method comprising the steps of:
- reacting an unsaturated carboxylic acid corresponding to the hydrophobic
30 group with an alkylene oxide corresponding to the oxyalkylene linking

group while maintaining the temperature of the reaction below that at which spontaneous polymerisation of the unsaturated groups of the hydrophobic group would occur; and.

5 phosphating the resultant polyalkoxylated hydrophobic group.

14. A method according to Claim 13 wherein the polyalkoxylation process step is carried out with the aid of a catalyst.

10 15. A method according to Claim 14 wherein the catalyst is a catalyst for alkoxylation which does not catalyse the polymerisation of unsaturated groups of the hydrophobic group.

15 16. A method according to Claim 14 or 15 wherein the catalyst for alkoxylation is a strong Lewis acid.

17. A method according to Claim 16 wherein the Lewis acid is boron trifluoride.

20 18. A method according to any one of Claims 14 to 17 wherein a small portion of a catalyst for alkoxylation is added to the unsaturated carboxylic acid before addition of the alkylene oxide.

25 19. A method according to any one of Claims 14 to 18 wherein a bulk portion of the catalyst for alkoxylation is added to the unsaturated carboxylic acid with the alkylene oxide.

30 20. A method according to any one of Claims 14 to 19 wherein a small portion of the catalyst for alkoxylation is added after completion of the addition of the alkylene oxide.

21. A method according to Claim 20 wherein hydroquinone is added to the reaction mixture after the addition of the small portion of catalyst.
22. A method according to any one of Claims 13 to 21 wherein any
5 unreacted alkylene oxide is removed.
23. A method according to Claim 22 wherein the alkylene oxide is removed by sparging with air.
- 10 24. A method according to any one of Claims 13 to 23 wherein the reaction of the unsaturated carboxylic acid and the alkylene oxide is carried out in an inert atmosphere.
- 15 25. A method according to any one of Claims 13 to 24 wherein the phosphation step is carried out by reaction with phosphorus pentoxide.
- 20 26. A method according to any one of Claims 13 to 25 wherein the product of the phosphation step is treated to remove any unreacted phosphoric acid.
27. A coating including a polymerisable surfactant according to any one of Claims 1 to 12 or made by the method of any one of Claims 13 to 26.
- 25 28. A coating according to Claim 28, which is an emulsion polymerisable coating.
29. A polymerisable surfactant substantially as described herein.

30. A method of making a polymerisable surfactant substantially as described herein.

31. A coating including a polymerisable surfactant substantially as
5 described herein.